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(54) Title: PREPARING STERILE ARTICLES FROM CERTAIN POLYMERS

(57) Abstract: A method of preparing a sterile article is disclosed. An article is prepared from a polymer into which is incorporated a stabilizer having the general formula: where each A is independently selected from E, OR, SR, and CO-R, and can join the aromatic ring to form an additional ring, E is R or R(OCH<sub>2</sub>R\*CH)<sub>R</sub>, G is E, CO-R, -C(E)H-O-R, C(OE)(H)-O-R, -C(E)(R\*")-R\*"-CO-OR, C(OE)(R\*")-E\*"-COOR, -C(OE)R\*"-O-R, -C(OE)HR, or -C(OE)R<sub>2</sub>, J is A, each R is independently selected from H, R', R'"COR', R'"COOR', R'"C(OR")R", or R'"C(OR")R"\*OR", each R' is independently selected from alkyl from C<sub>1</sub> to C<sub>24</sub>, aryl from C<sub>6</sub> to C<sub>24</sub>, alkaryl from C<sub>7</sub> to C<sub>24</sub>, and aralkyl from C<sub>7</sub> to C<sub>24</sub>, R" is H or R', R'" is alkylene from C<sub>1</sub> to C<sub>24</sub>, arylene from C<sub>5</sub> to C<sub>24</sub>, alkarylene from C<sub>7</sub> to C<sub>24</sub>, or aralkylene from C<sub>7</sub> to C<sub>24</sub>, m is 1 to 7, and n is 1 to 20. The article is exposed to gamma radiation; it yellows less after irradiation than it otherwise would.

# PREPARING STERILE ARTICLES FROM CERTAIN POLYMERS

#### Background of the Invention

This invention relates to the preparation of sterile articles from certain polymers. In particular, it relates to making the articles from poly(vinylchloride) (PVC) that contains a benzyl alcohol, cinnamyl alcohol, or geraniol-based stabilizer, then subjecting the article to ionizing radiation, particularly gamma radiation.

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Various polymers, including PVC, polyethylene, and polypropylene, are used to make medical devices and as packaging for food. Sterilization is required and can be accomplished by exposing the devices or packages to gamma radiation. However, the gamma radiation can degrade the polymers, making them unsuitable or less acceptable for certain applications. In the case of PVC, the yellowing of sterilized articles is the most notable physical change as the result of such degradation.

Benzyl alcohol, geraniol, and some of the related ethers were reported to enhance or help enhance the thermal stability of PVC. (L. L. Wood GB 1151108, CAN 71:92299; J. D. Collins, H. Coates, I. H. Siddiqui US 3,845,017; JP 55069609 CAN 93:151163). Benzyl alcohol and cinnamyl alcohol have also been used as solvents for biocides in PVC. (EP 168949 CAN 104:187573)

#### Summary of the Invention

I have discovered that when certain compounds based on benzyl alcohol, cinnamyl alcohol, or geraniol are incorporated into certain polymers and the polymers are made into articles and are sterilized with gamma radiation, substantially less yellowing occurs.

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Most of the stabilizers used in this invention are FDA approved additives for food use and could be used for food and medical applications.

#### <u>Description of the Preferred Embodiments</u>

The stabilizers used in this invention have the general formula:

$$(J)_{m} \xrightarrow{A} O G$$

$$(A) \qquad (B)$$

$$(J)_{m} \xrightarrow{A} \xrightarrow{A} O G$$

$$(D)$$

$$(E)$$

where each A is independently selected from E, OR, SR, and CO-R, and can join the aromatic ring to form an additional ring (e.g., α-hydroxyxanthene), E is R or R(OCH<sub>2</sub>R°CH)<sub>n</sub>, G is E, CO-R, -C(E)H-O-R, C(OE)(H)-O-R, -C(E)(R")R"-OR, -C(E)(R")-R"-CO-OR, C(OE)(R")-E"-COOR, -C(OE)R"-O-R, -C(OE)HR, or -C(OE)R<sub>2</sub>, J is A, each R is independently selected from H, R', R'"OR', R""COOR', R""C(OR")R", or R'"C(OR")R'"OR", each R' is independently selected from alkyl from C<sub>1</sub> to C<sub>24</sub>, aryl from  $C_8$  to  $C_{24}$ , alkaryl from  $C_7$  to  $C_{24}$ , and aralkyl from  $C_7$  to  $C_{24}$ ,  $R^*$  is H or R',  $R'^*$  is alkylene from  $C_1$  to  $C_{24}$ , arylene from  $C_6$  to  $C_{24}$ , alkarylene from  $C_7$  to  $C_{24}$ , or aralkylene from  $C_7$  to  $C_{24}$ , m is 1 to 7, and n is 1 to 20. Preferably, A is H and J is R, OR, or SR as those stabilizers are easier to make and more effective. Also, R is preferably alkyl from  $C_7$  to  $C_{24}$ , R' is preferably alkyl from  $C_1$  to  $C_{12}$ , R" is preferably alkyl from  $C_1$  to  $C_6$ ,  $R^{1*}$  is preferably alkyl from  $C_1$  to  $C_6$ , G is preferably H or benzyl, and m is preferably 1 for the same reasons. The preferred stabilizers are general formulas (A) and (C) as they are easier to make and less expensive. Example of stabilizers of formula (A) include 4-benzyloxybenzyl alcohol, benzhydrol, 9,10dihydro-9-anthracenol, 9-hydroxyxanthene, 9H-thioxanthen-9-ol, 1,2,3,4-tetrahydro-1-naphthalenol, benzyl ether, diveratryl ether, benzyl methoxyethyl acetal, (1R)-(-)nopol benzyl ether, 1,3-dibenzyloxy-2-propanol, benzyl benzoate, benzyl acetoacetate, benzyl phenylacetate, dibenzyl adipate, dibenzyl malonate, dibenzyl sebacate, benzyl butyl phthalate, poly(vinyl benzyl ether), poly(benzyl methacrylate), poly(methyl 4-benzyloxy-phenylsiloxane); Example of stabilizers of formula (B) include 1-naphthalenemethanol, 2-naphthalenemethanol,

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[(phenylmethoxy)methyl]naphthalene, 2-[(phenylmethoxy)-methyl]naphthalene, 1,1'-[oxybis(methylene)]-bis-naphthalene, 2,2'-[oxybis(methylene)]-bisnaphthalene, 1-naphthylmethyl acetate; Example of stabilizers of formula (C) include cinnamyl alcohol, -amyl cinnamyl alcohol, trans-2-methyl-3-phenyl-2-propen-1-ol, cinnamyl ether, benzyl cinnamyl ether, cinnamyl acetate, trans-cinnamyl butyrate, cinnamyl benzoate, cinnamyl phenylacetate, cinnamyl isovalerate, cinnamyl acid cinnamyl ester, poly(vinyl cinnamyl ether), poly(cinnamyl methacrylate), poly(methyl 4-cinnamyloxy-phenylsiloxane); Example of stabilizers of formula (D) include 3-(1-naphthyl)-2-propen-1-ol, 3-(2-naphthyl)-2-propen-1-ol, 3-(1-naphthalenyl)-2-propen-1-ol acetate, 3-(2-naphthalenyl)-2-propen-1-ol acetate; Example of stabilizers of formula (E) include geranlol, benzyl geranyl ether, geranyl hexanoate, geranyl phenylacetate, poly(vinyl geranyl ether), poly(geranyl methacrylate), poly(methyl 4-geranyloxy-phenylsiloxane).

Some of the stabilizers are commercially available as food additives. Those that are not commercially available can be made by techniques known in the art. For example, cinnamyl benzyl ether can be made by the benzylation of cinnamyl alcohol with benzyl chloride or benzyl bromide in the presence of a base.

The stabilizers of this invention are effective in reducing the yellowing of articles made from polymers such as PVC, polyvinylidene chloride, polyethylene, and polypropylene after exposure to ionizing radiation. The polymer can be made into any type of article, including medical devices, food packaging, and radiation protection devices.

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The polymer can be stabilized by the addition of about 0.005 to about 70 phr (parts by weight per 100 part by weight of the polymer) of the stabilizer to the polymer. Less stabilizer is less effective and more stabilizer offers little additional benefit. The preferred amount of stabilizer is about 0.2 to about 20 phr. The stabilizer can be added to a polymer in a variety of ways, such as mixing the reactants at the beginning or during polymerization. The stabilizer is preferably added after at least 70 wt% of the monomer has polymerized. The stabilizer can be added as a solid or with a solvent as a slurry or a solution. Common organic solvents such as N-methylpyrrolidone, diglyme, acetamide, acetone, methanol, ethanol, isopropanol, dimethylsulfoxide, or dimethylformamide can be used; water can also be used. Water miscible solvents, such as acetone, tetrahydrofuran, and methanol, are preferred. If the stabilizer is a solid, it is preferable to add it in a solvent as that achieves a more uniform distribution of the stabilizer in the polymer. The stabilizer can also be added to the polymer along with or as a shortstop, or during the drying or compounding of the polymer. Various methods can be used for compounding, including milling, dry mixing, and extrusion.

The following examples further illustrate this invention:

#### EXAMPLES 1 to 125

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To a mixture of 150.00 g PVC (sold by Occidental Chemical Corporation as "Oxy 240" or sold by Oxy Vinyls as "OV 30"), 0.30 g stearic acid (used as a lubricant), 0.23 g of a zinc and calcium mixed salts of mixed fatty acids (used as a

heat stabilizer; sold by Witco as "Mark 152 S"), 97.50g (less the amount of gamma ray stabilizer used) of dioctyl phthalate ("DOP," used as a plasticizer and to increase flexibility), 15.00 g epoxidized soy bean oil (used as an HCl scavenger to reduce degradation; sold by Witco as "Drapex 6.8"), was added a gamma ray stabilizer. The mixture was thoroughly blended and hot milled at 300°F (182°C) for 5 minutes. The resulting PVC sheet was cut and pressed into a 4"x3"x1/4" (10x8x0.6 cm) plaque at 330°F (182°C). The plaque was divided into two smaller pieces. One was saved for comparison and one was subjected to y radiation at a dose of 50 kGy. The irradiated piece was again divided into two pieces and one of these pieces was oven aged at 50°C for 48 hours. All of the samples were measured for yellowness index with a Macbeth 2020 Plus Color Eye Spectrometer, as described by the Hunter equations (see "The Measurement of Appearance" by Richard S. Hunter, John Wiley & Sons, New York, 1975). The following table gives the stabilizers used and the results.

1	_	

		Amount		Yellowness	
Example	Stabilizer	(g)	Initial	After	After
				Radiation	Aging
Control	none	none	19.1	55.4	79.9
1	Benzyl ether	0.5	16.2	42.9	65,1
2	44	1.0	17.0	37.0	57.2
Control	none	none	21.1	57.2	77.2
3	Benzyl ether	2.01	32.8	33.1	51.9
4	"	5.02	19.4	26.9	42.4
5	4	10.02	17.6	22.3	36.5
6	cc .	15.04	15.6	19.7	32.2
7	"	20.03	16.1	18.8	31
8	4	30.02	15.4	17.3	27.5
Control	none	none	17.1	52.3	84.4
9	Benzyl methoxyethyl acetal	0.5	17.9	42.1	66.1
10	ec	1.02	16.8		
11	44	1.5	16.5	35.1 34.6	58.9 54.5

		Tu	· · · · · · · · · · · · · · · · · · ·		<u>.</u>	
	12	4	2.02	15.4	29.7	50.5
	13	<u> </u>	2.52	17.2	27.8	47.8
	14	ű	3.02	16.5	27.5	45.2
	Control	none	none	19.3	55.7	75.4
5	15	Diveratryl ether	1.30	19.2	39.8	59.7
	16	4	3.50	20.6	33.2	50.8
	17	Benzyl cinnamyl ether	2.00	18.9	35.8	47.9
	18	et	4.00	17.1	30.5	37.8
	19	u	6.00	16.1	27.4	36.4
10	Control	none	none	19.1	55.4	79.9
	20	(1R)-(-)-Nopol benzyl ether	6.46	19.3	38.6	54.7
	21	и	12.92	16.7	34.8	47.0
	Control	попе	none	19.1	55.4	79.9
	22	1,3-Dibenzyloxy-2-propanol	0.51	17.5	49.3	70,7
15	23	4	1.02	16.6	44.4	64.3
	24	4	1.54	17.5	42.8	62.4
•	25	CE	2.03	17.4	39.8	60.3
	Control	none	none	18.1	50.2	75.5
	26	4-Benzyloxybenzyl alcohol	2.40	18.6	28.4	42.1
20	27	65	4.80	18.1	25.5	34.7
	Control	none	none	19.1	55.4	79.9
	28	9-Hydroxyxanthene	0.50	17.1	62.9	84.2
	29	u	1.00	18.4	51.4	72.7
	30	46	1.52	17.3	46.7	68.4
25	31	u	2.17	17.7	42.2	63.7
	Control	none	none	21.1	57.2	77,2
	32	Benzyl benzoate	2.01	18.6	45.7	65.3
	33	46	5.1	19.0	39.7	58.5
	34	и	10.01	18.7	34.3	51.8
30	35		15.03	18.1	29.9	47.2
	36	et .	20.19	18.9	31.7	50.5
	37		30.08	19.1	28.3	43.8
	Control	none -	none	19.1	55.4	79.9
	38	benzyl acetoacetate	4.88	17.9	34.1	46.1
<b>35</b>	39		9.72	23.0	31.0	42.4
	Control	none	none	21.1	57.2	77.2
	40	Dibenzyl malonate	2.70	16.9	29.4	
	41	44	6.43	17.8	30.8	45.3 48.6
	Control	none	none	19.3	55.7	75.4
40	42	Dibenzyl sebacate	3.05		39.9	
	43	4	6.06	18.8	34.2	59.4
	44	u	9.08		33.1	52.1
	Control	none		17.7		48.8
			none	19.3	55.7	75.4

			<u> </u>		•	
	45	Dibenzyl adipate	3,00	18.0	40.0	58.3
	46	<u> </u>	6.01	17.9	35.3	52.8
	47	cc .	9.02	21.1	32.0	47.8
	Control	none	none	19.3	55.7	75.4
5	48	Benzyl butyl phthalate	10.03	18.0	40.2	60.7
	49	· ·	20.03	18.1	35.8	53.7
	50	tt	30.05	18.8	32.5	48.3
	51	cc	40.04	18.5	32.0	46.6
	52	ш	50.02	18.7	30.6	45.0
10	53	4	60.06	20.1	29.2	43.6
	Control	none	none	17.1	52.3.	84.4
•	54	Dibenzyl phthalate	1.50	17.7	54.3	80.4
	55	44	4.29	15.0	47.7	70.9
	Control	none	none	17.1	52.3	84.4
15	56	Cinnamyl alcohol	0.54	17.0	37.6	62.5
	57	u	1.11	14.7	27.6	48.4
	58	· ·	1.53	17.2	27.5	42.8
	59	ti .	2.03	15.5	21.9	35.9
	60		2.6	16.9	23.6	34.7
20	61	46	3.09	14.6	20.0	31.5
	Control	none	none	17.1	52.3	84.4
	62	Alpha-amyl cinnamyl alcohol	0.51	18.7	56.9	77.3
	63	4	1.01	18.0	57.1	77.1
	64	u	1.5	17.6	57.6	74.2
25	65	u .	2.01	18.9	59.0	74.7
	66	EC.	2.5	19.3	57.7	72.8
	67	56	3.02	18.9	57.2	70.0
	Control	none	none	16.9	61.7	84.1
	68	Trans-2-methyl-3-phenyl-2-propen-	1.01	17.3	34.8	55.4
	<u></u>	1-ol		***	34.0	33.4
30	69	a	2.00	14.4	27.8	44.0
	70		3.00	16.3	24.2	37.8
	Control	none	none	19.3	55.7	75.4
	71	Cinnamyl ether	1.0205	19.7	44.1	55.9
	72		2.0412	20.7	37.1	
35	73	££	3.0637	18.8	33.1	46.4
	74	cc	5.1007	18.8	29.0	
	75	60	8.1642	18.2		36.3
	Control	none	none	19.3	29 <u>,2</u> 55.7	37.3
	76	Cinnamyl acetate	1.39	19.7	39.6	75.4
40	77	и	3.30	19.7		51.1
	Control	none	none		36.8	51.6
•	78	Trans-cinnamyl butyrate	1.00	16.6	49.1	52.5
			1.00	18.2	40.2	46.5

10		<b></b>		٠.			
SO		79	u .	2.02	175	75.5	38.7
State			<u>_</u>				
Section							37.5
Sa		82					38.1
Control   none   none   19.3   61.6   79	5	83	cı				36.3
10			none				34.3
85	•	84	Cinnamyl benzoate				79.0
10		85	u				64.4
Control   none   none   19.3   61.6   79		86	46				56.5
S	10	Control	none				52.8
SS		87	Cinnamyl phenylacetate				79.0
Section   Sect		88	"				56.9
Control   none   none   19.3   61.6   79		. 89	ш				49.7
15   90   Trans-cinnamyl isovalerate   19.3   61.6   79.		Control	none				46.8
100	15		<del></del>				79.0
101		100	u sissani, i isovalciate				58.5
Control   none   none   19.3   18.7   39.6   49.		101	61				52.6
102   Cinnamic acid cinnamyl ester   3.03   18.7   42.6   52.1			none				49.1
103						55.7	75.4
104	20		" Estate acid chinality i ester				52.0
Control   none   14.9   54.0   74.			«				45.9
105 Geraniol 0.49 14.2 48.1 67.1 106			none				45.1
106							74.7
25			u u				67.5
108 " 2.99 15.1 31.2 45.1 109 Geranyl hexanoate 1.01 17.5 45.2 73.3 111 " 1.01 17.5 45.2 70.7 113 " 2.02 18.6 42.2 67.8 114 " 7. 3.03 17.3 37.9 67.8 115 Geranyl benzyl ether 1.03 15.5 36.2 44.7 118 " 2.01 15.0 33.3 35.1 118 " 2.01 15.0 33.3 35.1 118 " 3.00 14.2 26.7 33.2 119 " 5.01 14.7 23.4 35.2 119 " 5.01 14.7 23.4 35.2 119 " 5.01 14.7 23.4 35.2 119 " 5.01 12.0 " 5.01 14.7 23.4 35.2 11.0 " 5.01 12.0 " 5.01 14.7 23.4 35.2 11.0 " 5.01 12.0 " 5.01 14.7 23.4 35.2 11.0 " 5.01 12.0 " 5	25		46				56.6
Control   none   15.1   31.2   45.1   109   Geranyl hexanoate   0.51   15.6   46.0   72.0   110   17.5   45.2   73.3   111   1.52   14.8   42.5   70.7   113   1.52   14.8   42.5   70.7   113   1.52   14.8   42.2   67.8   114   1.5   15.2   15.2   36.3   66.2   114   1.5   15.5   15.2   36.3   66.2   114   1.5   15.5   15.2   36.3   66.2   15.5   15.5   36.2   44.7   16.6   16.6   49.1   51.5   16.6   17.5   17			al				50.4
109 Geranyl hexanoate 0.51 15.6 46.0 72.0 110 " 1.01 17.5 45.2 73.3 111 " 1.52 14.8 42.5 70.7 113 " 2.02 18.6 42.2 67.8 114 " 2.5 15.2 36.3 66.2 114 " 2.5 15.2 36.3 66.2 114 " 3.03 17.3 37.9 67.8 115 Geranyl benzyl ether 1.03 15.5 36.2 44.7 116 " 2.01 15.0 33.3 35.1 118 " 2.01 15.0 33.3 35.1 118 " 3.00 14.2 26.7 33.2 119 " 5.01 14.7 23.4 33.2 119 " 5.01 14.7 23.4 35.2			Done				45.1
30						52.3	84.4
30			" HEXAHORIE				72.0
112 " 2,02 14.8 42.5 70.7  113 " 2,02 18.6 42.2 67.8  114 " , 3.03 17.3 37.9 67.8  Control none	30		"		17.5		73.3
113 " 2.02 18.6 42.2 67.8  114 " , 3.03 17.3 37.9 67.8  Control none  none 16.6 49.1 51.5  115 Geranyl benzyl ether 1.03 15.5 36.2 44.7  116 " 2.01 15.0 33.3 35.1  117 " 3.00 14.2 26.7 33.2  119 " 5.01 14.7 23.4 33.2  120 " 6.04 15.6 26.2 35.2			"		14.8	42.5	70.7
35			cc		18.6	42.2	67.8
35 Control none form none 16.6 49.1 51.5 115 Geranyl benzyl ethër 1.03 15.5 36.2 44.7 116 " 2.01 15.0 33.3 35.1 118 " 4.00 14.2 26.7 33.2 119 " 5.01 14.7 23.4 35.1 120 " 6.04 15.6 26.2 26.2 26.2 26.2 26.2 26.2 26.2 2					15.2	36.3	
35				3.03	17.3		
115 Geranyl benzyl ethér 1.03 15.5 36.2 44.7  116 " 2.01 15.0 33.3 35.1  117 " 3.00 14.2 26.7 33.2  119 " 4.00 14.2 26.1 33.2  119 " 5.01 14.7 23.4 35.1	35			none	16.6	49.1	
110   2.01   15.0   33.3   35.1   118   "   3.00   14.2   26.7   33.2   119   "   5.01   14.7   23.4   33.2   120   "   6.04   15.6   26.2   35.2	22		Geranyl benzyl ether	1.03	15.5	36.2	
40 120 " 3.00 14.2 26.7 33.2 118 " 4.00 14.2 26.1 33.2 120 " 5.01 14.7 23.4 35.1 120 " 6.04 15.6 26.2 25.2				2.01	15.0		
40 4.00 14.2 26.1 33.2 5.01 14.7 23.4 35.1 6.04 15.6 26.2				3.00	14.2		
40 120 " 5.01 14.7 23.4 35.1				4.00	14.2		
604 156 262 220	40			5.01			
	40			6.04			
Control none			none				
121 Geranyl phenylacetate 150 184 105		121	Geranyl phenylacetate				
122 " 1.30 18.4 40.5 47.3 3.00 15.7 35.1 40.2		122	66				

122	4.0				
123		4.50	16.2	29.9	35.5
124	"	6.02	15.3	30.2	22.2
125	44	7.02	1 1 2 2 -	30.2	3/.3
			16.0	31.2	33.5

As can be observed from the above table, after  $\gamma$  radiation the polymers that contained a stabilizer had significantly less discoloration than the control samples. The table also shows that ethers and alcohols are better at reducing yellowing than esters and can be used in lower amounts.

CLAIMS:

#### 1. A method of preparing a sterile article comprising

(A) producing a polymer selected from the group consisting of poly(vinyl chloride), poly(vinylidene chloride), polyethylene, and polypropylene, that contains about 0.005 to about 70 phr of a stabiliser having the general formula:

$$(J)_{m} \xrightarrow{A} \xrightarrow{A} G$$

$$(J)_{m} \xrightarrow{A} G$$

where each A is independently selected from E, OR, SR and CO-R, and can join the aromatic ring to form an additional ring, E is R or R(OCH<sub>2</sub>R"CH)<sub>n</sub>, G is E, CO-R, -C(E)H-O-R, C(OE)(H)-O-R, -C(E)R")R"''-OR, -C(E)(R")-R"''-CO-OR, C(OE)(R")-E"'-COOR, -C(OE)R"''-O-R, -C(OE)HR, or -C(OE)R<sub>2</sub>, J is A, each R is independently selected from H, R', R"''OR', R"''COOR', R"''C(OR")R", or R"''C(OR")R"''OR", each R' is independently

selected from alkyl from  $C_1$  to  $C_{24}$  alkaryl from  $C_7$  to  $C_{24}$ , and aralkyl from  $C_7$  to  $C_{24}$ , R" is H or R', R" is alkylene from  $C_1$  to  $C_{24}$ , arylene from  $C_6$  to  $C_{24}$  alkarylene from  $C_7$  to  $C_{24}$ , or aralkylene from  $C_7$  to  $C_{24}$ , m is 1 to 7, and n is 1 to 20;

- (B) making said article from said polymer, and
- (C) sterilising said article with ionising radiation.
- 2. A method according to Claim 1 wherein said polymer comprises poly(vinylchloride).
- 3. A method according to Claim 1 or 2 wherein A is H.
- 4. A method according to Claim 1, 2 or 3 wherein G is H or benzyl.
- 5. A method according to any one of Claims 1 to 4 wherein J is R, OR, or SR.
- A method according to any one of claims 1 to 5 wherein R is alkyl from C<sub>7</sub> to C<sub>24</sub>.
- A method according to any one of Claims 1 to 6 wherein said stabiliser has the general formula

$$(J)_{m}$$
 $A$ 
 $G$ 

8. A method according to any one of Claims 1 to 6 wherein said stabiliser has the general formula

 A method according to any one of Claims 1 to 6 wherein said stabiliser has the general formula

$$(J)_{m}$$
 $A$ 
 $A$ 
 $A$ 
 $G$ 

10. A method according to any one of Claims 1 to 6 wherein said stabiliser has the general formula

11. A method according to any one of Claims 1 to 6 wherein said stabiliser has the general formula

- 12. A sterile article prepared according to the method of any one of Claims 1 to 11.
- 13. A method preparing a sterile article comprising
  - (A) making poly(vinyl chloride) that contains about 0.2 to about 20 phr of a stabiliser having the general formula

where G is H or benzyl and J is R, OR, or SR, and R is alkyl from  $C_7$  to  $C_{24}$ .

(B) making said article from said poly(vinyl chloride), and

(C) sterilising said article with gamma radiation.

14. A method according to Claim 13 wherein said stabiliser has the formula

15. A method according to Claim 13 wherein said stabiliser has the general formula

 A method according to Claim 13 wherein said stabiliser has the general formula

17. A method according to Claim 13 wherein said stabiliser has the general formula

18. A method according to Claim 13 wherein said stabiliser has the general formula

- A sterile medical article prepared according to the method of any one of Claims 13 to 18.
- 20. A method of preparing a sterile medical article comprising
  - (A) making poly(vinyl chloride) that contains about 0.2 to about 20 wt % of a stabiliser having the general formula

where G is H or benzyl and each R is independently selected from alkyl from  $C_8$  to  $C_{12}$ ,

- (B) making said medical article from said poly(vinyl chloride), and
- (C) sterilising said medical article with gamma radiation.

### 21. A resin comprising

(A) a polymer selected from the group consisting of poly(vinyl chloride), poly(vinylidene chloride), polyethylene and polypropylene that contains about 0.005 to about 70 phr of a stabiliser having the general formula

$$(1)_{m} \xrightarrow{A} O G \qquad (1)_{m} \xrightarrow{A} O G \qquad (2)_{m} \xrightarrow{A} O G \qquad (3)_{m} \xrightarrow{A} A A A O G \qquad (4)_{m} O G \qquad (5)_{m} O G \qquad (5)_{m} O G \qquad (5)_{m} O G \qquad (5)_{m} O G \qquad (6)_{m} O G \qquad (6$$

where each A is independently selected from E, OR, SR, and CO-R, and can join the aromatic ring to form an additional ring, E is R or  $R(OCH_2R"CH)_n$ , G is E, CO-R, -C(E)H-O-R, C(OE)(H)-O-R, -C(E)(R")R"''-OR, -C(E)(R")-R"''-CO-OR, C(OE)(R")-E"''-COOR, -C(OE)R'''-O-R, -C(OE)HR, or  $-C(OE)R_2$ , J is A, each R is independently selected from H, R', R'''OR', R'''COOR', R'''C(OR")R", or R'''C(OR")R'''OR'', each R' is independently selected from alkyl from  $C_1$  to  $C_{24}$ , aryl from  $C_6$  to  $C_{24}$ , and alkaryl from  $C_7$  to  $C_{24}$ , R'' is H or R', R''' is alkylene from  $C_1$  to

 $C_{24}$ , arylene from  $C_6$  to  $C_{24}$ , alkarylene from  $C_7$  to  $C_{24}$ , or aralkylene from  $C_7$  to  $C_{24}$ , m is 1 to 7, and n is 1 to 20.

22. A stabiliser for use in stabilising a polymer, the stabliser having the general formula

where each A is independently selected from E, OR, SR and CO-R, and can join the aromatic ring to form an additional ring, E is R or R(OCH<sub>2</sub>R"CH)<sub>n</sub>, G is E, CO-R, -C(E)H-O-R, C(OE)(H)-O-R, -C(E)R")R"-OR, -C(E)(R")-CO-OR, C(OE)(R")-E"-COOR, -C(OE)R"-O-R, -C(OE)HR, or -C(OE)R<sub>2</sub>, J is A, each R is independently selected from H, R', R""OR', R""COOR', R""C(OR")R", or R""C(OR")R""OR", each R' is independently selected from alkyl from C<sub>1</sub> to C<sub>24</sub> aryl from C<sub>6</sub> to C<sub>24</sub>, and arlkyl

from  $C_7$  to  $C_{24}$ , R" is H or R', R" is alkylene from  $C_1$  to  $C_{24}$ , arylene from  $C_6$  to  $C_{24}$ , alkarylene from  $C_7$  to  $C_{24}$  or aralkylene from  $C_7$  to  $C_{24}$ , m is 1 to 7, and n is 1 to 20;

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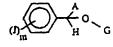
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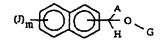
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(54) Title: PREPARING STERILE ARTICLES FROM CERTAIN POLYMERS





(57) Abstract: A method of preparing a sterile article is disclosed. An article is prepared from a polymer into which is incorporated a stabilizer having the general formula: where each A is independently selected from E, OR, SR, and CO-R, and can join the aromatic ring to form an additional ring, E is R or R(OCH<sub>2</sub>R"CH)<sub>n</sub>, G is E, CO-R, -C(E)H-O-R, C(OE)(H)-O-R, -C(E)(R")R"-OR, -C(E)(R")-R"-CO-OR, C(OE)(R")-E"-COOR, -C(OE)R"-O-R, -C(OE)HR, or -C(OE)R<sub>2</sub>, J is A, each R is independently selected from H, R', R"OR', R"COOR', R"C(OR")R", or R"C(OR")R"OR", each R' is independently selected from alkyl from C<sub>1</sub> to C<sub>24</sub>, aryl from C<sub>6</sub> to C<sub>24</sub>, alkaryl from C<sub>7</sub> to C<sub>24</sub>, and aralkyl from C<sub>7</sub> to C<sub>24</sub>, R" is H or R', R" is alkylene from C<sub>1</sub> to C<sub>24</sub>, arylene from C<sub>6</sub> to C<sub>24</sub>, alkarylene from C<sub>7</sub> to C<sub>24</sub>, or aralkylene from C<sub>7</sub> to C<sub>24</sub>, m is 1 to 7, and n is 1 to 20. The article is exposed to gamma radiation; it yellows less after irradiation than it otherwise would.



#### INTERNATIONAL SEARCH REPORT

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A. CLASSII IPC 7	FICATION OF SUBJECT MATTER COSK5/04 COSL27/06 A61L2/00	)	i
According to	o International Patent Classification (IPC) or to both national classific	ation and IPC	
	SEARCHED		
Minimum do IPC 7	cumentation searched (classification system followed by classification COSK A61L	on symbols)	
	ion searched other than minimum documentation to the extent that s		
	ata base consulted during the international search (name of data ba ternal, WPI Data	se and, where practical search terms used)	
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other	means ent published prior to the international filing date but han the priority date claimed	ments, such combination being obvious in the art.  *&* document member of the same patent if	
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